PHASE EQUILIBRIUM STUDY OF A PORTION OF THE SYSTEM TiO_2—Al_2O_3—SiO_2

BY

ANDREW TUNG-SHENG YEN

B.S., Yenching University, 1939
M.S., Yenching University, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CERAMIC ENGINEERING IN THE GRADUATE COLLEGE OF THE UNIVERSITY OF ILLINOIS, 1949

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INTRODUCTION

Titanium dioxide commonly occurs in fireclays in amounts of 1.5 to 2.0 percent. Although there has never been any comprehensive study made on the effect of titania in fireclay refractories, it is usually believed that its presence is not desirable. It is the purpose of this work to study fundamentally the effect of titania by conducting a phase equilibrium study of the three-component system TiO_2—Al_2O_3—SiO_2. Although equilibrium conditions are not generally attained in refractories, the phase relationships would indicate the trend or tendency of changes that may occur.

Studies were also conducted to determine the influence of iron oxide and soda in small percentages, when added to some of the ternary compositions. They are usually present in fireclays as minor constituents. It is interesting and important to see what their effects are.

EXPERIMENTAL PROCEDURE

The quenching method was chosen to conduct this phase equilibrium study of the TiO_2—Al_2O_3—SiO_2 system. The method has been described in detail in previous literature.[1] Chemically pure materials were used for sample preparations. Titanium dioxide was, however, prepared from titanium tetrachloride by hydrolysis. The samples were prepared with considerable care to insure that both equilibrium and homogeneity were attained in the mixtures. The process consisted of wet mixing, grinding, prefusing and regrinding to pass the 250-mesh sieve. This material was used in the subsequent quenching experiments. The crystalline phases present in the quenched samples were determined semi-quantitatively by their X-ray diffraction patterns,[2] using a Norelco Geiger-counter X-ray spectrometer.

DISCUSSION OF RESULTS

From the results of the quenching experiments, the fields of different primary phases, the boundary lines and two quintuple points in a large portion of the system have been established. The high titania and the high alumina ends of the system have, however, not been studied.

The primary phase fields are the cristobalite, the mullite, the rutile, the $Al_2O_3 \cdot TiO_2$ and the alumina fields. Of these, the mullite, the $Al_2O_3 \cdot TiO_2$ and the rutile fields cover more than three-fourths of the system and the cristobalite field is exceptionally small.

Of the two quintuple points that have been established, one is an eutectic point and the other is a peritectic point. The eutectic point, which involves the phases cristobalite, rutile and $Al_2O_3 \cdot TiO_2$, has a most probable composition of SiO_2 79.0%, Al_2O_3 7.5% and TiO_2 13.5% at 1477 $\pm$ 5°C. The peritectic point, at which the coexisting phases are cristobalite, mullite and $Al_2O_3 \cdot TiO_2$, has a most probable composition of SiO_2 79.5%, Al_2O_3 10.3% and TiO_2 10.2% at 1482 $\pm$ 5°C. A major part of the system has liquidus temperatures considerably above 1550°C.

From the phase diagram of this ternary system, it can be seen that the fluxing effect of titania is considerable, especially at higher temperatures. At 1540°C., a theoretically pure kaolinite clay would not have any glass formation. The addition of two percent titania would, however, cause the development of about forty percent of glassy phase at that temperature and five percent titania would cause the development of almost fifty percent.

The addition of two percent of iron oxide to some of the ternary compositions has very slight fluxing effect. The addition of two percent of soda has, however, a remarkable influence. Such addition of soda produces twenty to thirty percent of glassy phase at temperatures as low as 1300°C. It is the combined effect of alkalies with titania that is especially serious in fireclays.

BIBLIOGRAPHY

1. (a) E. S. Shepard, R. A. Rankin and F. E. Wright, "The Binary Systems of Alumina and Silica, Lime and Magnesia," Am. J. Sci., (IV) 28, 293-333 (1909).

   (b) G. W. Morey, "Phase Dagram, Boundary Study," J. Wash. Acad. Sci., 13, 326 (1923).

2. (a) Alphabetical Index of X-ray Diffraction Patterns, A.S.T.M., Philadelphia, Pa., August, 1945.

   (b) H. P. Klug, L. Alexander and E. Kummer, "Quantitative Analysis with the X-Ray Spectrometer," Anal. Chem., 20 (7), 607-609 (1948).

VITA

Andrew Tung-Sheng Yen was born in Shanghai, China, on February 10, 1918. He attended the elementary and high schools in Peiping, China, and graduated in 1935. He entered Tsinghua University, China, in the fall of the same year and transferred to Yenching University in 1937, where he received both his B.S. and M.S. degrees in 1939 and 1941 respectively. He then taught for one year as an instructor in Yenching University and for another year as a lecturer in China University. After this, he worked for three years as a ceramic engineer in K.M.A. refractory plant, China, and came over to this country in the fall of 1946. He entered the New York University, New York City, and stayed there for one year with a part-time teaching fellowship. He matriculated at the University of Illinois in September, 1947, as the recipient of a Graduate fellowship in that University.

He is a member of the American Ceramic Society and the American Chemical Society. He is also a member of Keramos, Sigma Xi, Phi Kappa Phi, Phi Kappa Epsilon and the Phi Tau Phi honorary societies.

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